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Polycarbosilane Elastomers via Chain-Internal and Chain-End Latent Crosslinking

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6. AUTHORS

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8. PERFORMING ORGANIZATION REPORT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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12. DISTRIBUTION AVAILIBILITY STATEMENT

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12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The abstract is below since many authors do not follow the 200 word limit

14. SUBJECT TERMS

elastomers, durable, solvent resistant, hybrid silicon materials, polycarbosilane, polycarbosilane materials

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Report Title

Polycarbosilane Elastomers via Chain-Internal and Chain-End Latent Crosslinking

ABSTRACT

The mission/objective of this work has been to identify a new class of hybrid polymers based on carbosilane/carbosiloxane chemistry, the objective being to create elastomers having excellent solvent resistance, high initial modulus, elasticity greater than 600%, and tensile strengths 2X greater than existing elastomers. Polymers have been synthesized and are being examined for their performance. All the required parameters for performance have been met excepting the tensile strength goal of 2X existing elastomers. While the project is now concluded from a funding perspective, we continue to examine the concept of dual latent crosslinking to achieve the tensile strength goal.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Two manuscripts are in preparation to describe the latest work being done here (work completed by Dr. Piotr Matloka and Ms. Paula Delgado). These papers will be submitted by the end of the year.

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

The research completed during the past 6 months will be presented once we have the final answer regarding the dual latent crosslinking concept fully examined. I will be using alternate funds (the Butler Endowment Funds) to continue to gather these data. The goal is to illustrate that hydrolytic internal latent crosslinking, followed by thermal, ring opening latent crosslinking, leads to significant enhancements in tenacity.

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

This research likely will be presented at the 2008 NATO sponsored metathesis materials conference to be held in Rumania. I have tentatively sent this title to them for consideration.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
Paula Delgado	0.50
Piotr Matkola	0.10
FTE Equivalent:	**0.60**
Total Number:	**2**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Fabio Zuluaga	0.10
FTE Equivalent:	**0.10**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
K. B. Wagener	0.12	No
FTE Equivalent:	**0.12**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
Zach Keane (now pursuing PhD at Bel	0.10
FTE Equivalent:	**0.10**
Total Number:	**1**

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	1.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	1.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	1.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	1.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Piotr Matkola
Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

5 **Elastomeric Polymers**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) Y

Foreign Countries of application (5g-2):

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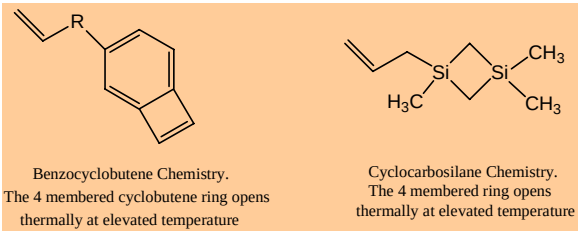


Benzocyclobutene Chemistry. The 4 membered cyclobutene ring opens thermally at elevated temperature

Cyclocarbosilane Chemistry. The 4 membered ring opens thermally at elevated temperature

Objective: The mission of our ARO supported research has been to identify new silicon/hybrid elastomer materials for use under highly demanding conditions.

Silicon-based elastomers offer advantages over pure hydrocarbon materials (greater elongation, better low temperature performance, higher operating temperatures, better weathering performance), yet carbon based materials predominate on the basis of greater tensile strength (2X that of silicones). A superior elastomer will merge these performance parameters via the creation of hybrid silicon/carbon-based materials.

What We Have Done. We have introduced the concept of latent crosslinking to meet this objective. Linear carbosilane/carbosiloxane polymers are prepared first (to achieve the desired object shape), followed by latent crosslinking both internally and at chain-ends to fix the article's shape and achieve maximum materials performance. Proof-of-principle research has been completed via fundamental structure/behavior investigations.

Two of our materials properties objectives have been met. We see a 3X increase in modulus, coupled with a 2.5X increase in elongation for these hybrid materials in comparison with commercial silicones. Tenacities are the same as commercial materials, values less than needed to meet our stated objective.

We note that ***these tenacities are less than 0.1% of the theoretical maximum possible*** for such polymers, based on bond dissociation energy analysis. Obviously the problem is not the strength of the polymer chain, but rather the interaction between polymer chains.

We attribute the less-than-desired tenacity performance to insufficient latent crosslinking. Apparently, the moisture driven latent crosslinking chemistry implemented here is not complete – moisture doesn't fully penetrate the hydrophoblic silicon hybrid polymer to induce sufficient crosslinking.

What We Have Done. The answer lies in chain-end latent crosslinking of a different nature, chemistry not driven by moisture.

We are implementing a dual-latent reaction concept to attack this tenacity challenge, using adduct forming chain-end latent crosslinks. The chain-end latent crosslinking reaction will be driven thermally, assuring complete conversion.

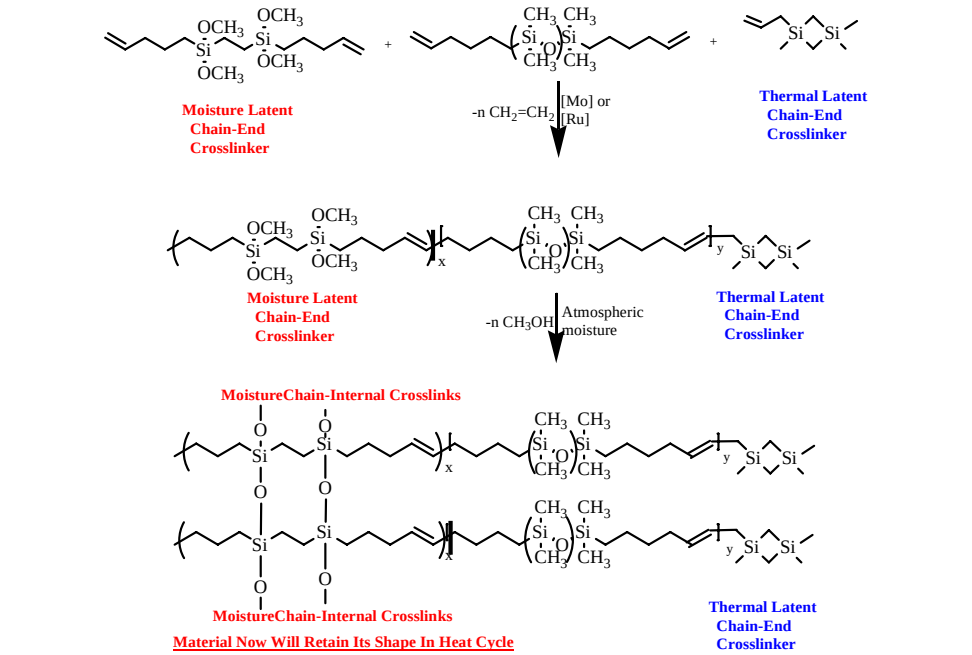
Two potential chain-end latent cross linkers are illustrated at the top of this report. The cyclocarbosilane structure is particularly relevant to this research, since they form adducts when opened (no small molecule released) and generate dimethyl silicon carbide structures.

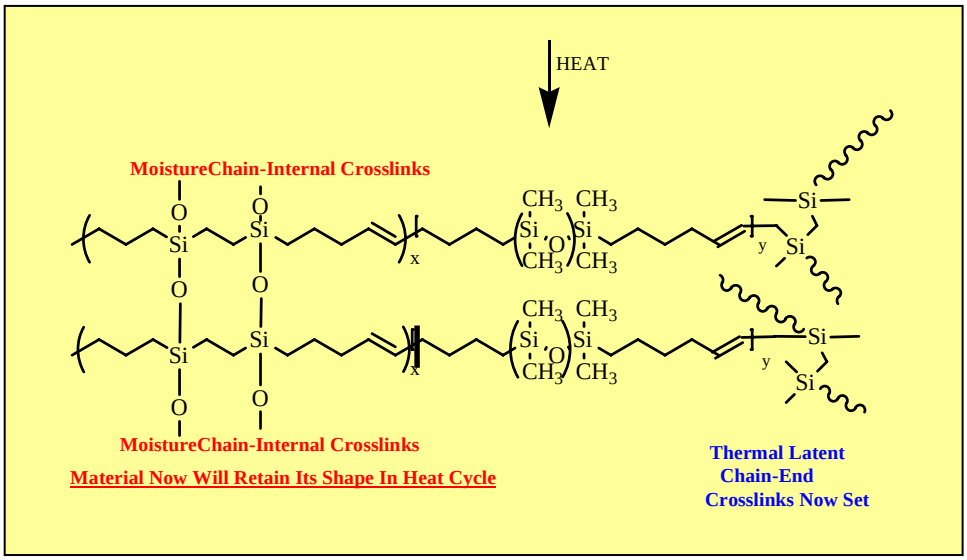
Simply invoking thermally driven crosslinking is not enough. Dual latent crosslinking is necessary. Otherwise, the strategic advantage we offer (being able to shape the desired object before crosslinking) would be lost; the linear polymer would soften and flow upon

exposure to heat before crosslinking took hold. Dual latent crosslinking is the key.

The existing moisture driven chain-internal chemistry first fixes the desired shape (so heat won't flow the polymer), then then a temperature ramp drives the thermal chain-end chemistry to crosslink the dangling chain ends. This chemistry is fully elucidated in the scheme below.

This dual latent crosslinking concept is fundamental in scope and is being investigated now. Should it prove beneficial, then we will expand the work towards investigation of silica-based fillers to achieve desired results.





Progress to End of Funding Period

A number of monomers have been prepared that possess the necessary moisture driven chain-internal and thermally driven chain-end crosslink sites. The repeat units also contain oxyethylene or carbosilane repeat units as required for elasticity.

The unique end-group thermal crosslinker 1-methyl-1-undec-10-enyl-silacyclobutane remains stable as a potential crosslink during all of the chemistry that preceds it. It is available for the last thermally driven reaction for network formation (as shown in the reaction chemistry illustrated above).

While the formal ARO funding process for this work is now concluded, we intend to continue the work using private funds available to the Principal Investigator. These private funds are being provided by the Butler Endowment fund within the George & Josephine Butler Polymer Research Laboratory.

The final step of this work will be casting of films for curing at temperatures in excess of 180 °C . We will complete these curing studies and gather the necessary mechanical performance data to see if we can achieve our strength goal, which is to exceed the typical silicon based elastomer tenacity by a factor of at least 2.